

Performance of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ Cathode Materials in Lithium Rechargeable Cells When Cycled up to 4.5 V

Meijing Zou,[†] Masaki Yoshio,[†] S. Gopukumar,^{*‡} and Jun-ichi Yamaki[§]

Department of Applied Chemistry, Saga University, Saga 840-8502, Japan, Central Electrochemical Research Institute (CSIR), Karaikudi-630 006, TamilNadu, India, and Institute of Advanced Materials Chemistry and Engineering, Kyushu University, Kasuga Koen 6-1, Kasuga 816-8580, Japan

Received August 1, 2004

Revised Manuscript Received December 9, 2004

Lithiated transition metal oxides, namely, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , are usually employed as cathode material in lithium ion batteries. However, among these materials, lithium cobalt oxide (LiCoO_2) is most widely used in the majority of commercial lithium ion cells owing to its ease of synthesis and high reversibility.¹ Even though the theoretical capacity of LiCoO_2 is around 273.8 mAh/g, practically only 0.5 mol of lithium is extractable; thereby, it delivers only ~137 mAh/g. Hence, to obtain higher capacities, one has to charge the cells to high voltages (4.5 V),² but such attempts have failed to produce stable LiCoO_2 due to structural changes³ during cycling. Therefore, many authors^{4,5} have attempted to improve the cycleability beyond 4.25 V by doping, but their methods resulted in only inferior capacities. Theoretical studies^{6,7} suggest that doping of LiCoO_2 with a transition metal ion leads to an increase in capacity whereas nontransition metal ion doping leads to an increase in voltage at the expense of capacity. To overcome the cycling problems at high voltages, Cho et al.^{8–10} recently coined the idea of coating LiCoO_2 with ceramic materials such as Al_2O_3 and ZrO_2 and succeeded in obtaining stable capacities for LiCoO_2 when cycled up to 4.5 V; this was also confirmed by Dahn et al.² Basically, doping involves the replacement of some cobalt sites with dopant ions in the lattice structure of the electroactive material, i.e., LiCoO_2 . However, in the case of coating the electroactive species or the materials are masked, thus preventing direct contact with the electrolyte solution. Recently, we also demonstrated the stable cycling up to 4.5 V of LiCoO_2 doped with either Mn¹¹ or Mg.¹² However, there

is no report on the stable cycling of doped LiCoO_2 at high voltages (4.5 V) involving metal ions such as Bi, Cr, Sn, and Zr. Hence, we decided to carefully synthesize doped LiCoO_2 involving Bi, Cr, Sn, and Zr as dopant ions and present in this communication the physical characterization and electrochemical performance of the synthesized materials for use in lithium rechargeable cells. Moreover, studies involving doping of LiCoO_2 with either Bi, Sn, or Zr have not been reported previously.

Doped LiCoO_2 of the type $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ incorporating one of the metal ions, viz., Sn, Cr, Bi, or Zr, has been prepared by mixing stoichiometric amounts of Co_3O_4 (>99.9% pure), Li_2CO_3 and $\text{Bi}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, $\text{Sn}(\text{CH}_3\text{COO})_2$ or ZrO_2 and melted in an argon atmosphere at 550 °C for 6 h and then cooled. The synthesized powders were ground and mixed well before finally annealing at 850 °C for 10 h, and then cooled, mixed, and subjected to repeated annealing for an additional 10 h. The synthesized mixture was cooled, mixed, and characterized physically and electrochemically.

The phase purity of the synthesized powders was analyzed using X-ray diffraction (XRD, Rint 1000, Rigaku) with $\text{Cu K}\alpha$ radiation. The surface morphologies of the synthesized powders were investigated using a scanning electron microscope (JSM-5300E, Japan Electron Ltd., Japan).

Analysis of electrochemical behavior of the synthesized powders was carried out using a two-electrode 2032 coin cell assembly. The aluminum cathode disk was coated with a mixture containing 85% of the active material mixed with 15% Teflonized carbon. The coating on aluminum foil was done by using the doctor blade technique and dried in an oven for 6–12 h at 120 °C. The dried sheet of the cathode material is then roll-pressed for increased adherence onto the aluminum foil current collector. Circular disks of the cathodes were then punched out and were used for fabricating the coin cells. The coin type cells were assembled in an argon-filled glovebox using the prepared circular disks of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ as the cathode, lithium (Cyprus Foote Mineral Co.) metal anode, and with Celgard 3401 as the separator using 1 M LiPF_6 in 1:2 by volume ethylene carbonate (EC)/dimethyl carbonate (DMC) [Ube Chemical, Japan] as electrolyte solution. The galvanostatic cycling studies of the fabricated cells were performed at a C/5 rate in the voltage range 3.5–4.5 V using an automatic battery tester at room temperature.

XRD patterns of the synthesized $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ [M = Cr, Bi, Sn, and Zr] are presented in Figure 1 and shows a strong Bragg peak located at $\sim 2\theta = 19^\circ$ and also medium intensity Bragg peaks at around 36 and 44°. Further, looking at the peak positions and intensities, we can easily index the patterns to a rhombohedral unit cell ($R\bar{3}m$) of a layered structure where all the fingerprint peaks, viz., 003, 101, 006, 102, 104, 108, and 110, are clearly assignable. The hexagonal lattice parameters, i.e., a and c were evaluated by using a

* Corresponding author. E-mail: deepika_41@rediffmail.com. Fax: +91-4565-227713.

[†] Saga University.

[‡] Central Electrochemical Research Institute (CSIR).

[§] Kyushu University.

- (1) Julien, C.; Gastro-Garcia, S. *J. Power Sources* **2001**, *97/98*, 290.
- (2) Chen, Z.; Dahn, J. R. *Electrochem. Solid-State Lett.* **2002**, *5* (10), A213.
- (3) Amatucci, G. G.; Tarascon, J. M.; Klein, L. C. *Solid State Ionics* **1996**, *83*, 167.
- (4) Jang, Y.; Haung, B.; Sadoway, D. R.; Ceder, G.; Chiang, Y. M.; Liu, H.; Tamura, H. *J. Electrochem. Soc.* **1999**, *146*, 862.
- (5) Tukamoto, H.; West, A. R. *J. Electrochem. Soc.* **1997**, *144*, 3164.
- (6) Ceder, G.; Chiang, Y. M.; Sadoway, D. R.; Ayginol, M. K.; Jang, Y. I.; Huang, B. *Nature* **1998**, *392*, 894.
- (7) Venkatraman, S.; Subramanian, V.; Gopukumar, S.; Renganathan, N. G.; Muniyandi, N. *Electrochem. Commun.* **2000**, *2*, 18.
- (8) Cho, J.; Kim, C.; Yoo, S. I. *Electrochem. Solid-State Lett.* **2000**, *3*, 362.
- (9) Cho, J.; Kim, Y. J.; Park, B. *Chem. Mater.* **2000**, *12*, 3788.
- (10) Cho, J.; Kim, Y. T.; Park, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3367.

(11) Zou, M.; Yoshio, M.; Gopukumar, S.; Yamaki, J. *Chem. Mater.* **2003**, *15*, 4699.

(12) Zou, M.; Yoshio, M.; Gopukumar, S.; Yamaki, J. *Electrochem. Solid State Lett.* **2004**, *7*, A176.

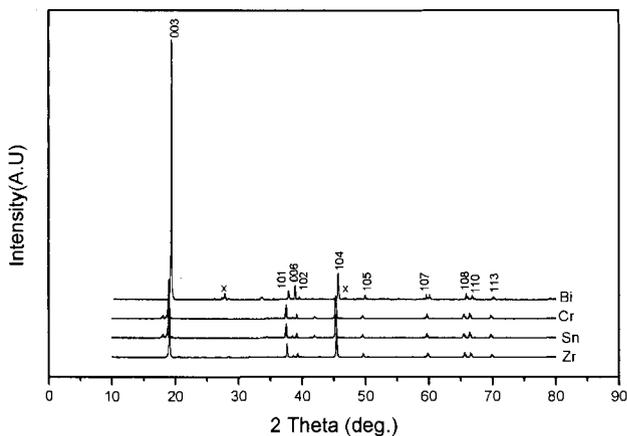


Figure 1. XRD patterns of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$.

Table 1. XRD Lattice Constants a and c and the c/a Ratio for Different Synthesized Doped LiCoO_2

material	a	c	c/a
$\text{LiBi}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.811	14.021	4.989
$\text{LiSn}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.815	14.035	4.987
$\text{LiZr}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.810	14.017	4.989
$\text{LiCr}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.816	14.028	4.982

least-squares fit and the c/a ratio, an indicator of metal–metal layering distance of the synthesized powders, are summarized in Table 1. It is observed that there are not many noticeable changes in the a parameter while the values of c show a very slight decrease than in the case of pristine LiCoO_2 .¹³ However, the c/a ratios in all the cases are higher than the critical value of 4.90 and the well-defined doublets of (006,102) and (108,110) indicate uniform ordering of lithium and transition-metal ions in the structure. It is interesting to observe that the XRD patterns of either Bi or Cr doped LiCoO_2 exhibits an abnormal increase in the 003 and 006 peaks, thereby suggesting a slight deviation from a perfect-layered structure.

Further, some impurity peaks are observed in the XRD patterns of $\text{LiBi}_{0.05}\text{Co}_{0.95}\text{O}_2$ materials. The abnormal increase in the 006 peak leads to an increase in the R -factor, i.e., the ratio of [006/102]/101 as suggested by Reimers et al.,¹⁴ and so results in the distortion of the hexagonal setting. Moreover, the abnormal intensity of the 003 peak may be ascribed due to the inhomogeneous distribution of the lithium and metal ions (Bi or Cr). These factors contribute to decreased electrochemical activity as will be seen elsewhere. However, in other cases of doping involving either Sn or Zr ions no such abnormality is observed and therefore confirms a perfect hexagonal setting. As can be seen, the XRD patterns of either $\text{LiSn}_{0.05}\text{Co}_{0.95}\text{O}_2$ or $\text{LiZr}_{0.05}\text{Co}_{0.95}\text{O}_2$ depict a perfect 006/102 and 108/110 doublet splitting similar to that of pristine LiCoO_2 ¹³ and therefore could be inferred to have perfect layering involving the metal ions and oxygen atoms. Further, the XRD patterns of $\text{LiSn}_{0.05}\text{Co}_{0.95}\text{O}_2$ exhibit few peaks due to impurities. Such kind of impurity has also been observed previously in the case of $\text{LiZn}_{0.5}\text{Co}_{0.5}\text{O}_2$.¹⁵

The surface morphology of the synthesized materials has been investigated using SEM. The analyses reveal that the

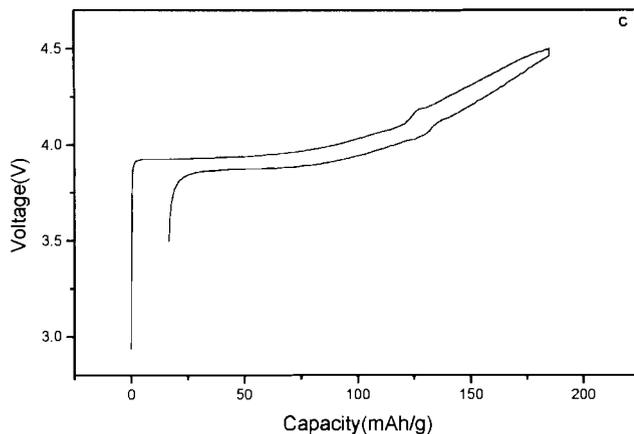


Figure 2. First charge/discharge patterns of $\text{LiZr}_{0.05}\text{Co}_{0.95}\text{O}_2$.

particle size is very large, i.e., more than $5\ \mu\text{m}$ in the case of Bi ion doping whereas the Sn ion dopant results in mixed morphologies with slightly smaller size ($3\ \mu\text{m}$). It is interesting to note that the morphologies of either Sn or Zr doped LiCoO_2 orient into very small particle sizes. Such kind of reduction in particle size indicates that the insertion or extraction of lithium ions could easily take place due to the reduction in diffusion path lengths, thereby enhancing the electrochemical activity.

Electrochemical performances of the fabricated 2032 lithium coin cell were evaluated by galvanostatically cycling the cells from 3.5 to 4.5 V. The cells incorporating Cr or Bi ions as dopants in LiCoO_2 exhibit an open circuit voltage (OCV) of around 2.4 V (vs Li metal) while Sn and Zr doped materials have higher OCVs, i.e., ~ 3.0 V.

A typical first charge/discharge pattern for a $\text{LiZr}_{0.05}\text{Co}_{0.95}\text{O}_2$ cell is depicted in Figure 2. It is observed that all the cells employing the present doping elements exhibit a high first charge of around 180 mAh/g with Cr exhibiting the highest. This is interesting considering the low OCV exhibited by this material. The irreversible capacities also depend on the type of dopant ions. Thus, the first cycle irreversible capacities in the case of Bi, Sn, and Zr are very small, around 10–15 mAh/g when cycled up to 4.5 V and hence could be potential materials for use in lithium ion batteries. Further, it is interesting to note that even though Cr doped materials exhibit the highest charge capacity (~ 197 mAh/g), at the same time they show maximum capacity fading in the very first cycle (~ 40 mAh/g), thereby suggesting poor cycleability at high voltages (4.5 V) despite showing no phase change at around 4.2 V. A comparison of the first charge and discharge profile of other doped materials, viz., Bi, Sn, and Zr, suggests the existence of two-phase oxidation/reduction and hence may lead to inferior capacities on extended cycling like in the case of pristine LiCoO_2 . Thus, we observe a phase change around 130–135 mAh/g in these materials, i.e., around 4.2 V. It is worthwhile to recall here that the XRD pattern of Bi-doped materials show unusual intensities of 003 and 006 peaks with additional impurity peaks marked “x”, thereby suggesting the coexistence of some secondary phases in this material. However, in the case of Sn- and Zr-doped materials such phase changes are

(13) Gopukumar, S.; Jeong, Y.; Kim, K. B. *Solid State Ionics* **2003**, *159*, 223.

(14) Reimers, J. N.; Rossen, E.; Jones, C. D.; Dahn, J. R. *Solid State Ionics* **1993**, *61*, 335.

(15) Julien, C.; Camacho-Lopez, M. A.; Mohan, T.; Chitra, S.; Kalyani, P.; Gopukumar, S. *Solid State Ionics* **2001**, *135*, 241.

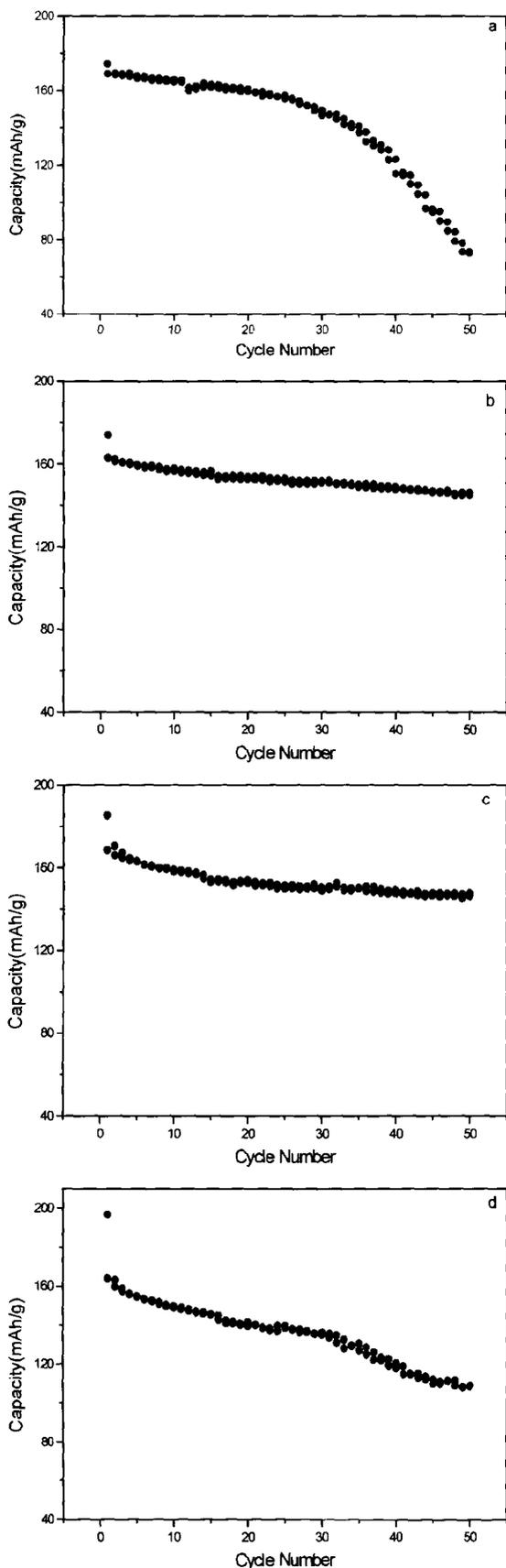


Figure 3. Galvanostatic cycling at $C/5$ rate in the voltage range 3.5–4.5 V of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$, $M =$ (a) Bi, (b) Sn, (c) Zr, and (d) Cr.

noticeable but the intensity of the 006 peak is minimized and so the phase change observed around 4.2 V vanishes after the first two or three cycles; hence, these materials are expected to deliver stable capacities on high voltage cycling.

Therefore, the synthesized powders were subjected to extended galvanostatic cycling studies (50 cycles) in the voltage range 3.5–4.5 V so as to ascertain the observed initial high capacities.

The galvanostatic cycling of the synthesized doped cathode materials in a lithium rechargeable 2032 type coin cell were investigated in the voltage range 3.5–4.5 V at $C/5$ rate and their performances are presented in Figure 3a–d. It can be seen from the figures that the cells employing either Cr or Bi ions as dopants (Figures 3a and 4d) show initial discharge capacities of around 160 to 170 mAh/g, but these fade subsequently on cycling and they retain a capacity of approximately 110 and 70 mAh/g respectively at the end of 50 cycles. Such fading has also been observed by other authors in the case of LiCoO_2^3 and is usually ascribed to the different phase changes taking place on extended high voltage cycling. However, it is interesting to note in the present studies that despite Cr-doped materials exhibiting the highest first charge capacities and also the absence of phase change at around 4.2 V, the cycleability is very poor at higher voltages (4.5 V). On the other hand, Sn- or Zr-doped material (Figures 3b and 3c) exhibited excellent cycleability over the investigated 50 cycles and deliver the highest stable capacities of around 150 mAh/g despite showing marginal phase changes at 4.2 V. Hence, we can say that cycleability can be improved by doping with Zr^{4+} dopants possibly by decreasing the Co^{4+} ions during oxidation. These results can be supported by the fact that the addition of minor amounts of tetravalent titanium to either LiNiO_2^{16} or LiCoO_2^{13} results in high capacities when cycled between 3 and 4.25 V. Further, looking at the cycleability of $\text{LiZr}_{0.05}\text{Co}_{0.95}\text{O}_2$, we observe not only good stable capacities delivered at high voltage cycling (4.5 V) but at the same time delivery of the highest capacities of ~ 155 mAh/g. This result looks very interesting as, to our knowledge, this is the first time such stable high voltage capacities are obtained even though some authors suggest improved performance up to 4.5 V range involving only a coating of LiCoO_2 .⁸ The present obtained results are superior in view of the high capacities obtained in a narrow voltage range of 3.5–4.5 V as compared to values of ~ 165 mAh/g reported by Cho et al.,⁸ in the voltage range 2.75–4.4 V employing a coating^{8–10} technique.

We may therefore conclude that in the present communication we have developed a novel technique for synthesizing doped LiCoO_2 materials resulting in enhanced stable capacities at high voltages (4.5 V). Moreover, we demonstrate for the first time that the material involving $\text{LiZr}_{0.05}\text{Co}_{0.95}\text{O}_2$ is a promising cathode material for use in lithium rechargeable cells delivering capacities of ~ 155 mAh/g at the $C/5$ rate when cycled in the voltage range between 3.5 and 4.5 V. This enhanced performance could be ascribed to the presence of some Co^{2+} ions due to charge compensation effect.¹³

Acknowledgment. S.G.K. thanks Kyushu University, Japan, for offering a visiting professorship and to Central Electrochemical Research Institute, Karaikudi, India, and CSIR, New Delhi, India, for grant of leave.

CM0487340